Electric Supplemental Information for:

Tuning the Dimension of the POM-based Inorganic-organic Hybrids from 3D Self-penetrating Framework to 1D Poly-pendant Chain *via* Changing POM Clusters and Introducing Secondary Spacers†

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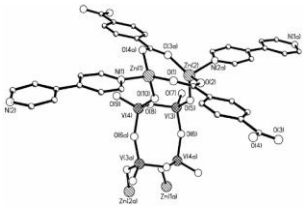
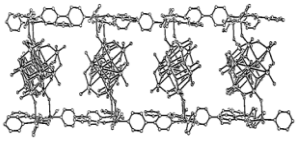
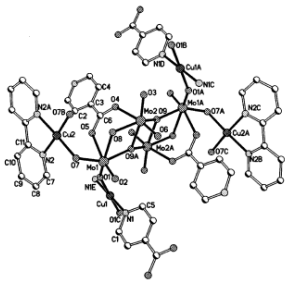
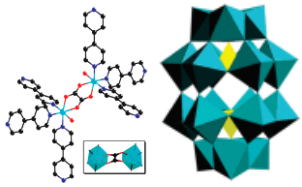
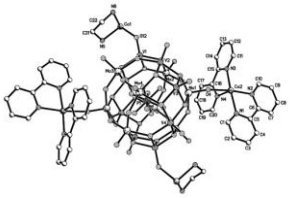
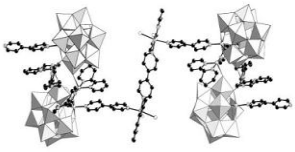
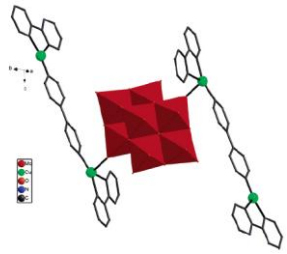
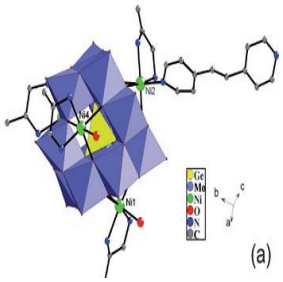
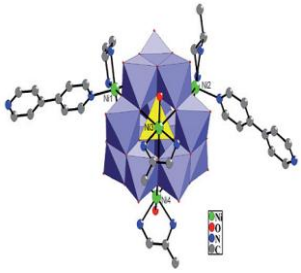
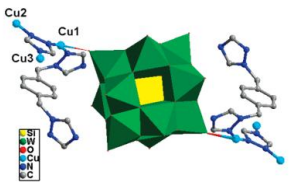
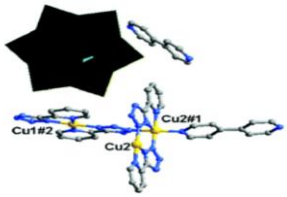
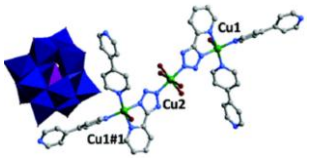
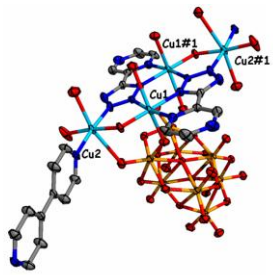
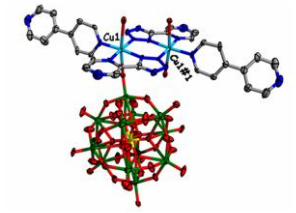
Table S1 Summarization of typical POM-based hybrids constructed by mixed-ligands

Compounds	Ligands 1 and 2	Types of mixed-ligands	References
 $[Zn_2(tp)(4,4'\text{-bpy})V_2O_6]$	tp 4,4'-bipy	**I**	*Tong and Chen et al.*, ***J. Chem. Soc., Dalton Trans.*** 2001, 770
 $[Cu(4,4'\text{-bpy})(nic)(H_2O)]_2Mo_8O_{26}$	nic 4,4'-bipy	**I**	*Lu et al.*, ***Chem. Mater***. 2002, 14, 2649
 $[\{Cu^{II}(2,2'\text{-bpy})\}\{Cu^{II}(IN)_2\}\{Mo_4O_{12}(OH)_2\}]$	IN 2,2'-bipy	**I**	*Wang et al.*, ***Inorg. Chem.*** 2003, 42, 6956
 $[Ni_2(4,4'\text{-bipy})_3(H_2O)_2(ox)][P_2W_{18}O_{62}]_2(H_2 4,4'\text{-bipy})\cdot H_2O$	ox 4,4'-bipy	**I**	*Liu and Su et al.*, ***Inorg. Chem.*** 2008, 47, 7133
 $[Co(en)_2][Co(2,2'\text{-bipy})_2]_2\text{-}[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$	en 2,2'-bipy	**II**	*Zhang and Zhu et al.* ***Chem. Commun***. 2002, 1416
 $[4,4'\text{-Hbipy}][\{Cu_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})_{2.5}\}$	2,2'-bipy 4,4'-bipy	**II**	*Dolbecq et al.* ***Dalton Trans.*** 2005, 3919

-$PW_{11}CuO_{39}]\cdot 16H_2O$			
 $K[\{Cu^{I}(2,2'\text{-bipy})\}(4,4'\text{-bipy})$ $-\{Cu^{I}(2,2'\text{-bipy})\}_{0.5}]_2[Mo_8O_{26}]$	2,2'-bipy 4,4'-bipy	**II**	*Wang et al.*, ***Cryst. Growth Des.*** 2006, 6, 2693
 $[GeMo^{V}_{8}Mo^{VI}_{4}O_{36}(\mu_2\text{-}OH)_4\{Ni(pda)(H_2O)\}_2$ $-\{Ni(pda)\}\{Ni(pda)(bpe)\}(bpe)_{0.5}]$ (**1**)  $[GeMo^{V}_{8}Mo^{VI}_{4}O_{36}(\mu_2\text{-}OH)_4\{Ni(pda)\}_2$ $-\{Ni(pda)(4,4'\text{-bpy})_{0.5}\}\{Ni(pda)(4,4'\text{-bpy})\}]$ $\cdot 7H_2O$ (**2**)	pda bpe	**II**	*Xu et al.*, ***CrystEngComm***. 2009, 11, 2488
 $[Cu_6(trz)_2(bbtz)_2(SiW_{12}O_{40})]$	trz bbtz	**III**	*Peng and Su et al.*, ***Cryst. Growth Des.*** 2010, 10, 1104
 $[Cu_3(2\text{-pytz})_4(4,4'\text{-bpy})][H_2SiMo_{12}O_{40}]$	2-pytz 4,4'-bipy	**III**	*Yan et al.*, ***Dalton Trans.***, 2013, 42, 1667

 $[Cu_3(2\text{-pytz})_2(4,4'\text{-bpy})_4(H_2O)_6]$ $\text{-}[H_4SiW_{12}O_{40}]_2\cdot 6H_2O$			
 $Cu_4(pzta)_2(4,4'\text{-bipy})(H_2O)_4(OH)_2$ $\text{-}[Mo_8O_{26}]\cdot 2H_2O$  $[Cu_2(pzta)_2(4,4'\text{-bipy})_2(H_2O)_2]$ $\text{-}[HPW_{12}O_{40}]\cdot 8H_2O$	pzta 4,4'-bipy	**III**	This work

The abbreviations in the table: tp = terephthalate, 2,2'-bipy = 2,2'-bipyridine, 4,4'-bipy = 4,4'-bipyridine, nic = nicotinic acid, IN = isonicotinateion, ox = oxalic acid, en= ethylenediamine, pda = 1,2-propanediamine, bpe = 1,2-bis(4-pyridine)-ethane, trz = 1-H-1,2,4-triazole, bbtz = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene, 2-pytz = 5-(2-pyridyl)tetrazolate, pzta = 5-(2-pyrazinyl) tetrazole.

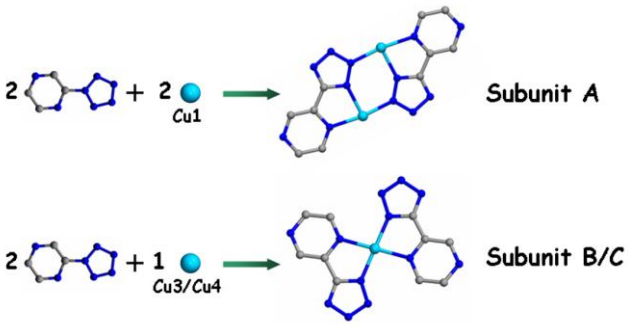


Fig. S1 The two kinds of TMCs in **1**.

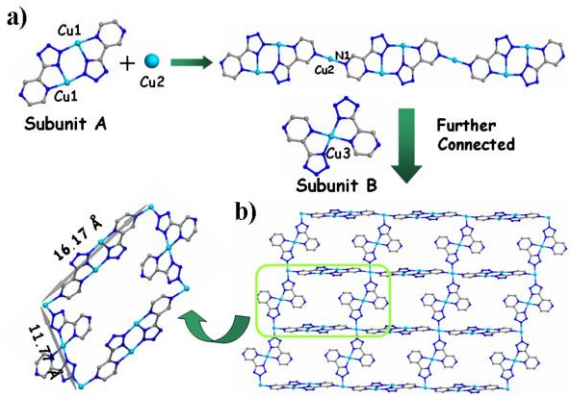


Fig. S2 (a) Ball/stick representation of subunit A, subunit B, infinite organic-inorganic hybrid chain formed by subunit A and Cu2, (b) 2D layers formed by subunit B further connected in **1**.

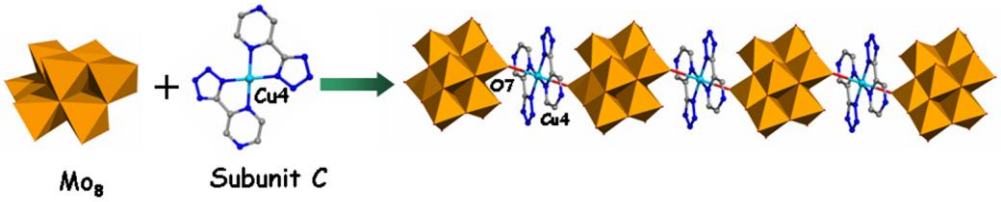


Fig. S3 Ball/stick representation of subunit C, infinite organic-inorganic hybrid chain formed by β-Mo_8 anions and subunit C.

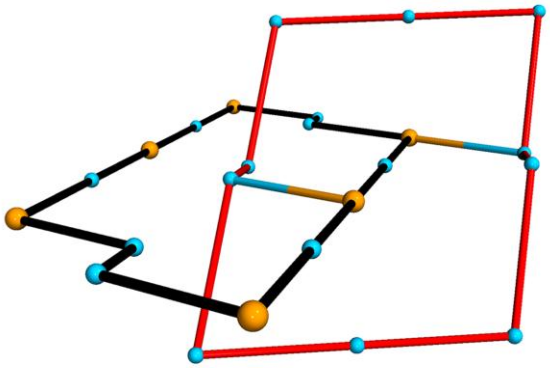


Fig. S4 The detailed view of the self-penetrating structure in **1**.

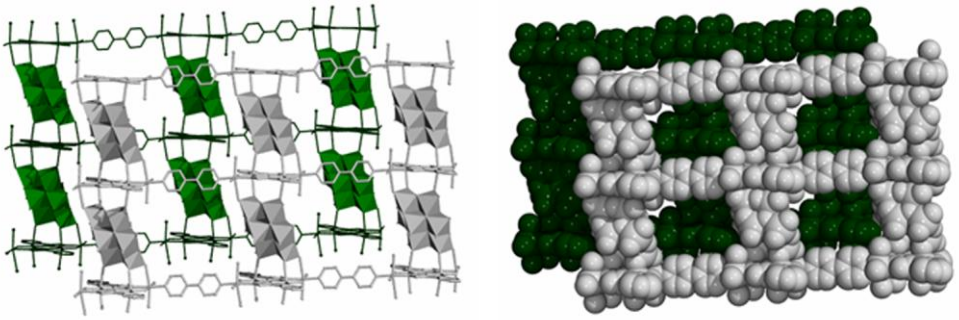


Fig. S5 View of the interdigitated structure in **3**.

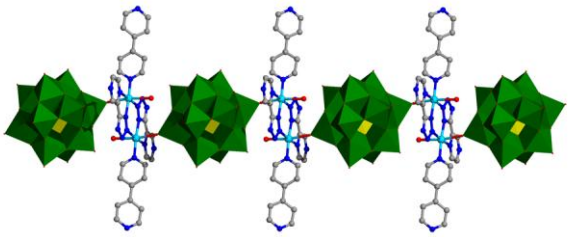


Fig. S6 Combined polyhedral/ball/stick representation of the infinite 1D Poly-pendant chain.

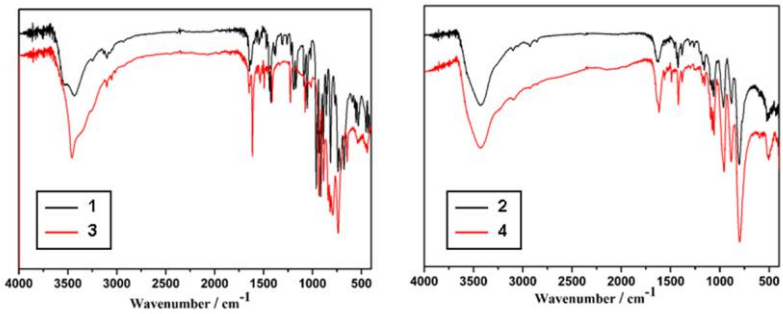


Fig. S7 The IR spectra of compounds **1-4**.

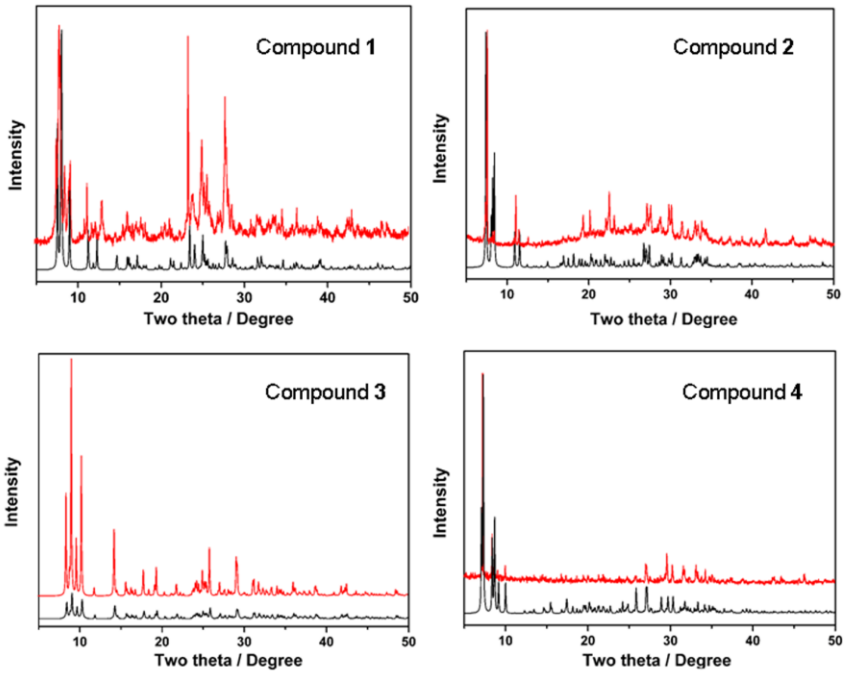


Fig. S8 The simulative (black) and experimental (red) powder X-ray diffraction patterns for **1-4**.

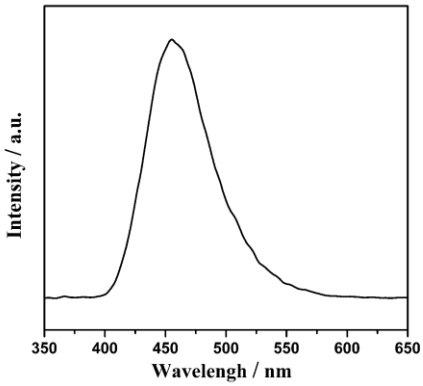


Fig. S9 Solid-state emission spectra of pzta ligand at room temperature.

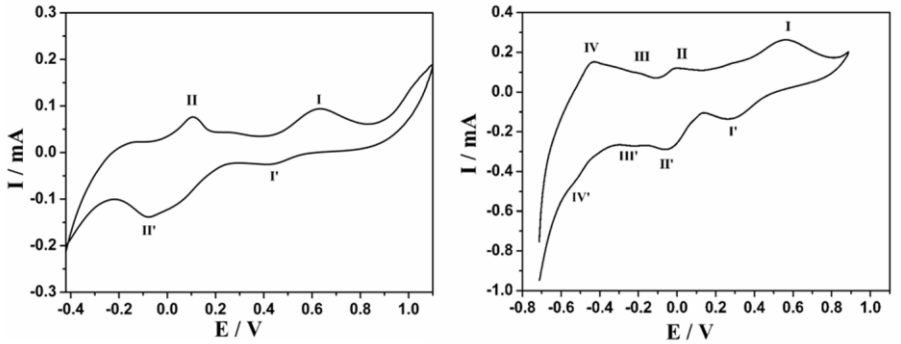


Fig. S10 The CVs of **1**-CPE (left) and **2**-CPE (right) in the 1 M H_2SO_4 solution at the scan rate of 50 $mV \cdot s^{-1}$.

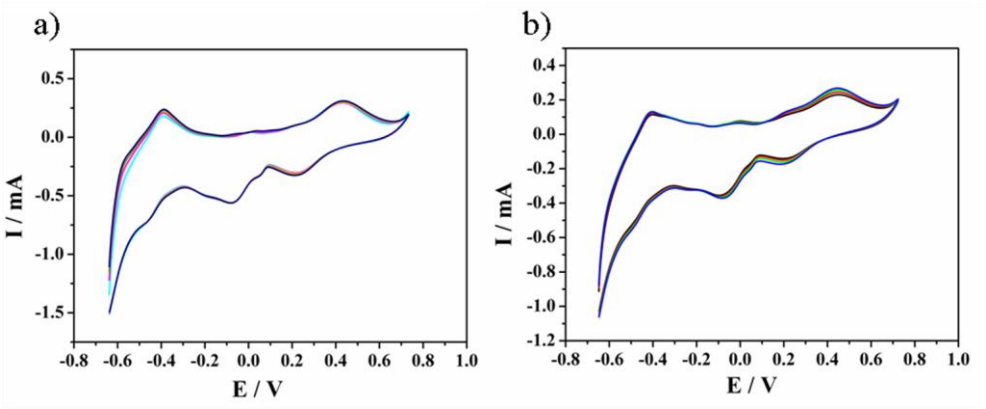


Fig. S11 (a) Reduction of H_2O_2 and (b) oxidation of AA for **2**-CPE in 1M H_2SO_4 solution (scan rate: 50 $mV \cdot s^{-1}$). The concentrations (from inner to outer) are 0.0, 10, 20, 30 mM for H_2O_2 and 0.0, 0.1, 0.2, 0.3 mM for AA.